

Oxidation of Alkenes with Use of Phase Transfer Catalysis¹

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ABSTRACT AND SUMMARY

The use of phase transfer catalysis (PTC) as an aid in the oxidation of long chain olefins with aqueous potassium permanganate (KMnO_4) in neutral and alkaline media and with aqueous ruthenium tetroxide (RuO_4) is reported. The phase transfer catalysts (PTCT) were either quaternary ammonium halides or crown ethers. The long chain olefins studied were 1-pentadecene, 9-octadecene, and methyl oleate. PTC not only increases the rate of these reactions but also gives good yields of reaction products. For example, *cis*-9-octadecene in methylene chloride reacted with aqueous KMnO_4 to give either dihydroxyoctadecane (80%) or pelargonic acid (80%), depending upon pH, when tetrabutylammonium bromide was used as the PTCT. When RuO_4 in conjunction with a PTCT was used as the oxidant, a quantitative yield of myristic acid was obtained from 1-pentadecene. The RuO_4 oxidant was conveniently regenerated in situ from RuO_2 and sodium hypochlorite. This regeneration is facilitated with a PTCT.

INTRODUCTION

Recent years have witnessed the ascendance of a new technique in organic chemistry in which reactions conducted in an aqueous-organic two phase system are improved by the presence of an ammonium or phosphonium salt or a crown ether (1-3). The general term applied to this method of facilitating two-phase reactions, which normally proceed either slowly or not at all, is phase transfer catalysis (PTC). PTC promotes these heterogeneous reactions by transferring the water soluble reactant into the organic phase where reaction with the organic soluble substrate occurs. Reactions improved by the application of PTC include: the generation of dichlorocarbene (4), the alkylation of carbonyl and related compounds (5), nucleophilic substitution reactions (6), and the oxidation of alkenes by aqueous potassium permanganate (7-10). The latter studies found that α -olefins are quantitatively oxidized by neutral aqueous potassium permanganate to carboxylic acids containing one less carbon atom than the starting olefin had, when the reactions are carried out with either a crown ether (7) or quaternary ammonium salt (8,10). With cycloalkenes, such as cyclohexene, diacids were obtained in high yields (8). The hydroxylation of cyclic olefins to *cis*-diols with basic potassium permanganate and quaternary ammonium phase transfer catalysts (PTCT) has also been investigated (9).

In view of the experimental difficulties encountered in the non-phase transfer catalyzed oxidation of water-insoluble internal olefins with aqueous potassium permanganate (11,12), we undertook the present investigation to determine if these reactions could be facilitated by PTC. We also studied the oxidative cleavage of olefins to carboxylic acids with ruthenium tetroxide with the aid of PTC. Ruthenium tetroxide is conveniently generated in situ from ruthenium dioxide by action of an oxygen donor, such as sodium metaperiodate or sodium hypochlorite (13); these oxidants also regenerate RuO_4 from any RuO_2 produced during the

oxidation. This regeneration of spent oxidant is facilitated by PTC.

EXPERIMENTAL PROCEDURES

Materials

cis-9-Octadecene was prepared by the lithium aluminum hydride reduction of the tosylate of oleyl alcohol (14). Purity as determined by gas liquid chromatography (GLC) and thin layer chromatography (TLC) was 98%. 1-Pentadecene (99%), methyl oleate (98%), tetrabutylammonium bromide, cetyltrimethylammonium bromide and dicyclohexyl-18-crown-6² were obtained from Eastman Chemical Company (Rochester, NY). Ruthenium dioxide² (45%) was obtained from Engelhard Industries. Sodium hypochlorite solution (5.75%), Chlorox, was purchased at a local supermarket.

Oxidations with Potassium Permanganate

Neutral potassium permanganate: A solution of KMnO_4 (30 mmole) in H_2O (50 ml) was placed into a 250 ml Morton flask equipped with a magnetic stirrer, addition funnel, and condenser. A solution of tetrabutylammonium bromide (3 mmole) in CH_2Cl_2 (30 ml) was added to the flask, and the two phases were vigorously stirred for 1 hr at 5-10 C. 9-Octadecene, 1a, (10 mmole) was added dropwise to the stirred reaction mixture over a 15 min period at 10 C. The mixture was then stirred for 12 hr at room temperature. The precipitated MnO_2 was reduced by bubbling SO_2 through the reaction mixture, and the mixture was acidified to pH 2 by the addition of conc. HCl. The CH_2Cl_2 layer was separated from the aqueous layer, and the latter was extracted with CH_2Cl_2 (2 x 25 ml). The combined organic layers were washed with H_2O (3 x 25 ml), dried over MgSO_4 and the solvent removed in vacuo. The crude oxidation product, after esterification with $\text{BF}_3 \cdot \text{MeOH}$ reagent, was analyzed by GLC (Table I). Products were identified by comparison with authentic samples by both GLC and TLC.

The bulk of methyl pelargonate, 2a, was then removed by distillation. Upon cooling, the yellow pot residue solidified. Recrystallization from petroleum ether gave yellow crystals of 9,10-diketooctadecane, 3, mp 54.4-55 C; IR: 1710 cm^{-1} ; mass spectrum: m/e, 282 (M^+), 141 (100%). From the filtrate, pure 9-keto-10-hydroxy-octadecane, 4, was isolated by preparative TLC on silica gel (benzene- Et_2O -MeOH, 95:5:1); IR: 3400 and 1710 cm^{-1} , mass spectrum: m/e, 284 (M^+).

Basic potassium permanganate: Into a 250 ml Morton flask equipped with a magnetic stirrer, addition funnel, and condenser was placed a solution of 9-octadecene (10 mmole), and tetrabutylammonium bromide (3 mmole) in CH_2Cl_2 (50 ml), and 50 ml of aqueous sodium hydroxide solution (40%). The stirred two phase reaction mixture was cooled to 0 C, and a solution of KMnO_4 in H_2O was added dropwise over a period of 1.5 hr. When addition was complete, the reaction mixture was allowed to warm and was stirred at room temperature for 12 hr. The precipitated MnO_2 was reduced by reaction with SO_2 , the mixture was acidified with conc. HCl, and the organic layer was sepa-

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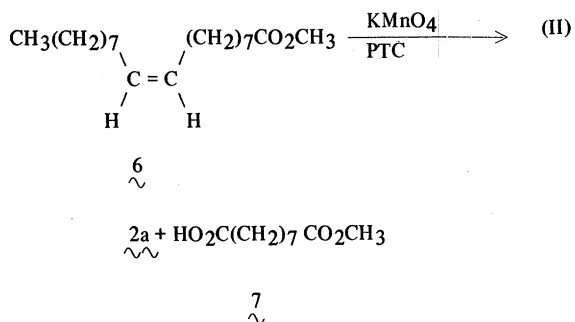
² Proper precautionary measures should be exercised when handling crown ethers and ruthenium tetroxide in view of their poisonous nature and strong oxidizing properties.

Other reports have shown that changes in reaction solvent and PTCT can markedly affect the course of phase transfer catalyzed reactions (16,17). We also studied changes in the above two variables to determine if the yields of **2a** could be improved. A change of solvent from benzene to CH_2Cl_2 with CTAB catalyst (exp 2, Table I) increased the yield of **2a** to 70% with a concomitant decrease in yields of byproducts **3** and **4**. This result agrees with the general principle that chlorinated hydrocarbons are generally the best solvents for carrying out phase transfer catalyzed reactions. With CH_2Cl_2 as solvent and a change of PTCT from CTAB to tetrabutylammonium bromide (TBAB), the yield of **2a** improved to 80% (exp. 3, Table I). When benzyltrimethylammonium bromide was used in place of CTAB, poorer yields of **2a** were obtained and the amount of byproducts **3** and **4** increased. Similar variations in yields of oxidation cleavage products with

changes in ammonium salt structure have been noted by Herriott (16). In general, Herriott found that an onium salt must have the proper hydrophobic-hydrophilic balance to be an efficient PTCT. This balance is generally found when the total number of carbon atoms about the nitrogen atom is in the range of C₁₆–C₂₀. Below this range the partition coefficient of the onium salt favors the aqueous phase, whereas much above this range (e.g., tetradecylammonium bromide) emulsification problems complicate the reaction procedure. An additional factor affecting PTCT activity is the structure of the onium salt catalyst. Symmetrical onium salts are generally more efficient PTCT than are unsymmetrical onium salts with approximately the same carbon number (compare TBAB with CTAB, exp. 2 and 3, Table I).

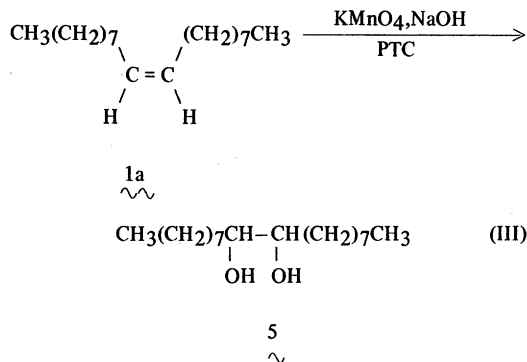
Another commonly used class of PTCT is the crown ethers (8,10). These catalysts, in contrast to the onium salts, are neutral macrocyclic ethers that transfer KMnO₄ into the organic phase by complexing potassium ion. When dicyclohexyl-18-crown-6 was substituted for TBAB and CH₂Cl₂ was used as solvent for the oxidation of *cis*-9-octadecene with KMnO₄, an 80% yield of pelargonic acid **2a** was obtained (exp. 4, Table I). In contrast, with benzene as the solvent in the above reaction, the yield of **2a** was similar to that obtained with CTAB in benzene. This again points out that CH₂Cl₂ is a better organic phase than benzene for conducting phase transfer catalyzed reactions. TBAB and the crown ether are comparable in facilitating the oxidation of **1a** to **2a** (exp. 3 and 4 in Table I). It would appear that the onium salts are the preferred catalysts for the phase transfer catalyzed oxidation of alkenes to carboxylic acids, because of higher cost of the crown ethers and their potential toxicological side effects.

To apply PTC to fatty esters, the oxidation of methyl oleate **6** with aqueous KMnO₄ was studied. The PTC system employed was CH₂Cl₂ solvent and TBAB catalyst, eq. II. The crude oxidation product, after esterification, was analyzed by GLC. The latter showed the presence of the expected cleavage products methyl pelargonate **2a** (67%) and monomethyl azelate **7** (72%). The crude product also showed evidence of other oxidation products, presumably the diketone and ketol derivatives, but these were not conclusively identified.



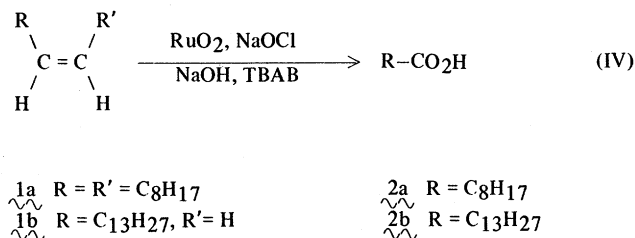
In addition to the oxidations carried out in neutral medium, we also investigated the phase transfer catalyzed oxidation of **1a** with KMnO₄ in alkaline medium. KMnO₄ oxidation of **1a** at higher pH favors *cis*-hydroxylation of **1a** to its *erythro* dihydroxy isomer **5**, eq. III. We obtained the best yields of **5** with dicyclohexyl-18-crown-6, in CH₂Cl₂ solvent as the phase transfer catalyst (exp. 7, Table I), eq. III. Of the onium salts studied, CTAB gave the poorest yield of **5** while TBAB gave intermediate yields of **5** (exp. 5 and 6, Table I). When we changed the solvent from CH₂Cl₂ to benzene, the crown ether gave a 10% yield of diol **5**, the remainder being unreacted olefin. This result again points out the importance of solvent selection in performing phase transfer catalyzed reactions. The phase transfer catalyzed hydroxylation of *cis*-9-octadecene with basic KMnO₄ occurs because of the ability of the onium salts and the crown

ethers to transfer both hydroxide ion and permanganate ion into the organic phase. The transfer of hydroxide ion into the organic phase is important, since the mechanism of hydroxylation of alkenes with KMnO₄ has been shown to require hydroxide ion (18).



Attempts to hydroxylate methyl oleate using the basic KMnO₄ procedure gave us poor yields (<25%) of the dihydroxy derivative. This result was probably due to the saponification of the ester which resulted in serious emulsion problems during the course of the reaction.

An alternative method for oxidizing alkenes uses ruthenium tetroxide as the oxidant. Ruthenium tetroxide (RuO₄) is a very powerful oxidizing agent which is soluble in a variety of hydrocarbon solvents (19). For example, a performed solution of RuO₄ in carbon tetrachloride rapidly oxidizes cyclohexene and 1-octene to adipaldehyde and heptaldehyde (20), respectively. More recently, it has been claimed that when alkenes are oxidized with RuO₄ formed in situ from RuO₂ and sodium hypochlorite and no organic solvent is used, carboxylic acids are the major product (21,22). We have not been able to reproduce the results obtained in the previous work (21). So, we reexamined this reaction by studying the oxidation of *cis*-9-octadecene, **1a**, and 1-pentadecene, **1b**, with ruthenium tetroxide generated in situ by the reaction of sodium hypochlorite with RuO₂, eq. IV.



Reaction of **1b** with RuO₂-sodium hypochlorite solution for 6 hr gave poor yields (<10%) of the expected myristic acid, **2b**. Aside from recovered **1b** other products formed in this reaction were identified as the dichloro- and chlorohydrin derivatives of **1b**. The latter two addition products resulted from the reaction of **1b** with chlorine and hypochlorous acid formed by the disproportionation of sodium hypochlorite. To suppress the formation of chlorinated byproducts, we repeated the experiment with added base, NaOH (exp. 1, Table II). We obtained a 33% yield of **2b** and observed no chlorinated byproducts. In a second experiment when we used carbon tetrachloride as solvent for **1b**, the yield of **2b** decreased to 10% (exp. 2, Table II). Since we were unable to obtain good results using the reported procedures, we decided to see if PTC would facilitate this reaction.

In the above two-phase system, the oxidation of **1b** by ruthenium tetroxide occurs in the organic phase. The ruthenium dioxide precipitate formed in this process then migrates to the interface where it is reconverted to

ruthenium tetroxide by the cooxidant which remains in the aqueous phase. Accordingly, vigorous mixing of the phase is required to obtain reasonable yields in short reaction times. Transferring hypochlorite anion into the organic phase should facilitate the rapid reoxidation of RuO_2 to RuO_4 and thus accelerate the rate of oxidation of 1b. We conducted reaction of 1b with RuO_2 -sodium hypochlorite oxidant with the PTCT tetrabutylammonium bromide in CH_2Cl_2 solvent (exp. 3, Table II). This cleavage of 1b to 2b was quantitative within the same reaction time period as those of experiments in the absence of PTC (compare exp. 3 and 4, Table II), and vigorous mixing of the reactants was not required. More importantly, in the absence of the RuO_2 oxidant, we recovered 1b intact. Additionally, we achieved quantitative conversions of 1b to 2b within the same reaction times as when we increased the molar ratio of 1b to RuO_2 from 1:6 to 32:1 (exp. 4, Table II). Higher molar ratios of 1b to RuO_2 could be used but these reactions required longer reaction times. In those experiments in which we used RuO_2 in catalytic amounts, the actual oxidant being consumed is sodium hypochlorite. The overall reaction of an alkene with the catalytic RuO_2 -hypochlorite system requires a stoichiometry of 4 moles of NaOCl per mole of alkene. To ensure complete oxidation of the double bond, we employed the actual molar ratio of 6:1 NaOCl to alkene.

Application of the phase transfer catalyzed RuO_4 - NaOCl oxidation technique to 9,10-octadecene resulted in lower yields of pelargonic acid 2a, during the same reaction time used for 1-pentadecene (compare exp. 4 and 5, Table II). However, the conversion of 1a to 2a increased when we employed longer reaction times (exp. 5-7, Table II). An important aspect of this oxidation reaction is the complete absence of byproduct formation as compared to the KMnO_4 oxidation procedure.

The oxidation of water-insoluble alkenes by KMnO_4 or RuO_4 has been facilitated by PTC and high yields of reaction products were obtained. The application of PTC to the above methods of oxidation offers several advantages over

conventional procedures. For example, the experimental procedures are relatively simple in that neither water-miscible solvents nor the preparation of oil/water emulsions are required. Neither high dilution techniques nor control of pH are needed to ensure good yields. The reaction products are isolated easily.